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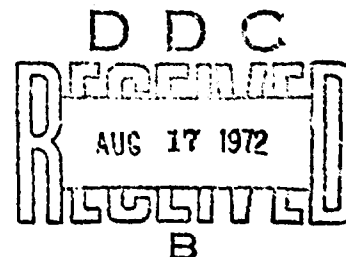
**SURFACE SEGREGATION STUDIES IN ALLOYS USING
AUGER ELECTRON SPECTROSCOPY**

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13. ABSTRACT <p>Several metals used in the nuclear field are found to be lacking in one or more respects when these metals are employed in their pure or unalloyed state. For a variety of reasons, minor alloying additions are often added to these pure metals. However, the basic role played by these alloying elements is not well understood. By utilizing the technique of Auger electron spectroscopy on zircaloy-2 and zircaloy-4, it has been possible to make correlations between observed surface phenomena (of both impurity and alloy species) and previously established mechanical properties, such as a strain rate sensitivity around 300°C in the zircaloys, and also chemical properties such as the build-up of an oxide layer above 300°C in these same zirconium alloys.</p>			

Surface Segregation Studies in Alloys Using Auger Electron Spectroscopy

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Several metals used in the nuclear field are found to be lacking in one or more respects when these metals are employed in their pure or unalloyed state. For a variety of reasons, minor alloying additions are often added to these pure metals. However, the basic role played by these alloying elements is not well understood. By utilizing the technique of Auger electron spectroscopy on zircaloy-2 and zircaloy-4, it has been possible to make correlations between observed surface phenomena (of both impurity and alloy species) and previously established mechanical properties, such as a strain rate sensitivity around 300°C in the zircaloys, and also chemical properties such as the build-up of an oxide layer above 300°C in these same zirconium alloys.

Introduction

In past years the technique of Auger electron spectroscopy (AES) has been used in a fundamental manner in several laboratories in this country and abroad by people interested in the nature of solid surfaces from a basic physics (or chemistry) viewpoint. Only recently has this method begun to emerge as an analytical tool with an eye toward solving practical problems.¹⁻³ Many of the stimuli for the more widespread use of this method have come from the fields of materials science and metallurgy. In these areas long standing problems in oxidation and corrosion, epitaxy and thin film growth, nucleation, diffusion, and fractography are now being approached, admittedly from a different viewpoint, but most certainly with renewed interest.

A natural outgrowth of basic Auger studies on pure materials⁴ has been the detection and identification of the various contaminants found to segregate on the surfaces and at the grain boundaries of pure metals. Along these same lines, it would seem logical to extend this surface impurity segregation phenomenon and investigate the basic role played by elements present as minor alloying additions in a multicomponent material. The purpose of this paper is to examine the effects, from a surface viewpoint, of adding small amounts of alloying elements to pure materials and to attempt to correlate these effects with other previously observed properties.

I. Experimental

Most of the early Auger spectroscopy work was carried out in three or four-grid low-energy electron

diffraction (LEED) systems operating not as LEED units but rather as ultrahigh vacuum retarding potential energy analyzers.⁴⁻⁹ However, much of the more recent work has utilized the newly developed cylindrical mirror analyzers.¹⁰ All data reported here were produced using a coaxial cylindrical analyzer. The particular analyzer employed was similar to that described previously,¹⁰ except that a double focusing model was constructed to improve resolution.¹¹ A grazing incidence side electron gun operated between 1.5 and 2.5 keV with approximately 50- μ A current in a 1 mm or less diameter spot size was used to excite the Auger transitions. Modulating voltages were typically 1-2 V rms at 7 kHz.

All samples were flat rectangular polycrystals and the faces studied all had areas between 1 and 2 cm². Spectroscopically pure argon was used in the sputtering experiments, with the ion pump turned off as soon as argon was introduced into the chamber as well as during the actual bombardment process. All sputtering treatments utilized 500-eV argon ions, while the total currents and times for each individual bombardment varied and are specified in the respective figure captions.

Auger spectra reported for specific temperatures were taken after the samples were resistance heated to and attained the given temperatures, held at those temperatures for 30 sec in each case, and then cooled back down to room temperature. Once back at room temperature and the pressure back in the 10⁻¹⁰-Torr range (usually from 1 to 2 min after shutting off the sample heater current), the Auger electron spectra characteristic of the reported temperatures were recorded.

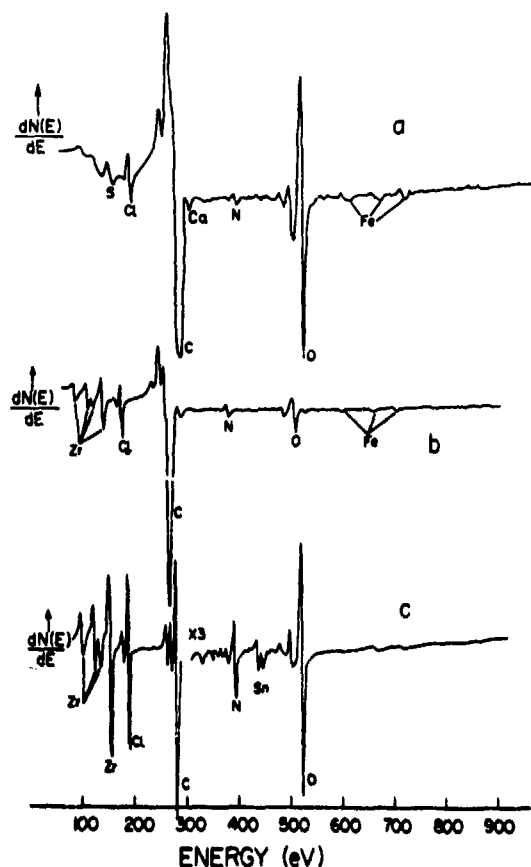


FIGURE 1. Auger spectrum $dN(E)/dE$ vs E for zircaloy-2 in the as-received condition. (a) Room temperature; (b) 300°C; (c) 500°C.

II. Results and Discussion

Primarily, two alloys were examined during the course of this study. They were zirconium alloys, those known as zircaloy-2 and zircaloy-4. Both zircaloy-2 and zircaloy-4 contain nominally 1.5% Sn. In addition to enhancing the corrosion properties of the zirconium matrix, the Sn also serves as a mechanical strengthener without adversely affecting the favorable nuclear properties of the zirconium. Zircaloy-2, along with the 1.5% Sn, also contains 0.15% Fe, 0.10% Cr and 0.05–0.10% Ni; the trace amounts of these elements are all added to stabilize the corrosion behavior. Zircaloy-4, in addition to the 1.5% Sn, contains 0.20–0.25% Fe and 0.10% Cr with very little or no nickel. The nickel is not present in zircaloy-4 since it was felt that it increased the absorption of hydrogen generated during the corrosion process and it is well-known that high hydrogen content in zirconium-base alloys reduces tensile ductility considerably. And indeed it has been shown that the modified alloy zircaloy-4 absorbs only one-half to one-third the hydrogen normally picked up by zircaloy-2 without otherwise altering corrosion behavior or mechanical properties.¹² It is interesting to note that the sum of the Fe plus Cr plus Ni contents for zircaloy-2 is very

nearly equal to the sum of the Fe plus Cr contents for zircaloy-4.

The remainder of this paper will be devoted to detailing the surface behavior of these two alloys with regard to the trace alloying additions and impurities and then attempting to relate these findings with other known properties of the same materials.

A. Zircaloy-2

In the as-received condition the contaminants detected on the surface of zircaloy-2 at room temperature were as follows: carbon, oxygen, chlorine, nitrogen, and small amounts of sulfur and calcium. Of the various alloying elements (namely, Sn, Fe, Cr, and Ni) present in this alloy, the only one detected on the sample surface prior to heating was Fe. No Sn, Cr, or Ni were found. These findings are presented in Fig. 1(a). The presence of the various surface impurities referred to above is not surprising in the light of earlier work done in this laboratory on pure zirconium.¹ Further heating of zircaloy-2 to above 300°C accomplished the following, as seen in Fig. 1(b): The oxygen concentration on the surface was drastically reduced, iron and nitrogen were still present in very small amounts with a somewhat noted increase in calcium and chlorine concentrations. As is shown in Fig. 1(b), the Auger peaks from the zirconium matrix were in evidence at 300°C. Carbon was still present at these temperatures, and it can be noted that the shape of the carbon Auger peak in Fig. 1(b) begins to show the formation of the metal carbide as changing from the carbon peak in Fig. 1(a) which is indicative of free carbon, perhaps in the form of graphite.¹³ It was not until zircaloy-2 was heated to around 500°C that any of the other minor alloying constituents begin to show on the surface. At this temperature, as shown in Fig. 1(c), tin became evident while the iron was virtually all gone as far as the surface was concerned. Carbon was now present as a carbide while Cl, S, Ca, N, and the Zr peaks had also increased proportionately. Oxygen was now (at 500°C) present in larger amounts than was shown at 300°C by Fig. 1(b), possibly indicating that above 300°C oxygen began to migrate or diffuse from the bulk to the surface. The removal of oxygen between room temperature and 300°C is presumably a simple desorption process. Subsequent heating to 700°C showed a further increase in all the peaks present in Fig. 1(c) except for oxygen at 510 eV which was reduced again, and Ca which was totally absent. Continued heating at 700°C reduced the size of the 272-eV carbon peak, indicating carbon was being removed from the surface. At 800°C, the sulfur and chlorine peaks had become quite large and iron had again appeared on the surface along with first evidence for the presence of Ni.

A dramatic change in the zircaloy-2 Auger spectrum occurred upon heating the samples in the temperature range 850–900°C. Nitrogen was totally removed and oxygen was reduced to the level of the alloying element tin. Spectra at 950°C showed only a large increase in sulfur over those taken between 850–900°C. Between 950 and 1000°C, effectively all tin, oxygen, and carbon were removed from the surface simultaneously. The bulk of chlorine present (as evidenced by the 185-eV Cl peak) had also been removed and now the 175-eV Zr peak was detected easily. Above 1000°C, the only contaminant present in zircaloy-2 surfaces was sulfur. It was not possible to remove sulfur from zircaloy-2 surfaces by simple heating alone in ultrahigh vacuum.

The only method found effective in removing sulfur from zircaloy-2 was argon-ion bombardment, as shown in Fig. 2(a). Note the absence of chlorine but the presence of large carbon and oxygen peaks, indicating the presence of these contaminants in the bulk. The purity of the argon used and the fact that the ion pump power was off during sputtering virtually rule out the possibility of these contaminants (i.e., C and O) being introduced as a result of the bombardment process. Only very little Sn could be detected in the room temperature spectrum of Fig. 2(a); no Fe, Cr, or Ni was found. It should be recalled here that Fe was found on the surface of the as-received zircaloy-2 at room temperature. Very small amounts of Fe were found upon heating the bombarded samples to 300°C. Heating to 500°C, the sputtered samples showed slight increases in Sn and Fe surface content and a somewhat larger increase in surface carbon content. At 700°C, as before, the carbon peak decreased, but appreciable amounts of Sn (especially), Fe and Ni were now evident, as seen in Fig. 2(b). Between 700 and 750°C sulfur began to come to the surface on the bombarded samples, much the same as for the nonbombarded ones. At 900°C, carbon and oxygen were greatly reduced and, for the first time on zircaloy-2 samples, chromium was detectable, see Fig. 2(c). Nickel was also present. These samples contained twice as much Cr as Ni, yet of these two elements Ni seemed to segregate preferentially on the surface.

It is of interest to compare other physical properties of alloys with the surface phenomena determined using Auger spectroscopy. Lee¹⁴ and Lee, Koch, and Rogers¹⁵ have documented a ductility minimum at certain strain rates for zircaloy-2 between 300° and 350°C. From the results of this Auger spectroscopy study, it has been shown [Figs. 1(b) and 1(c)] that the maximum concentration of carbon on the surface occurs at these temperatures and furthermore, this is the temperature range where surface carbon starts forming a metal carbide rather than being present as free carbon. And since most metal carbides are quite

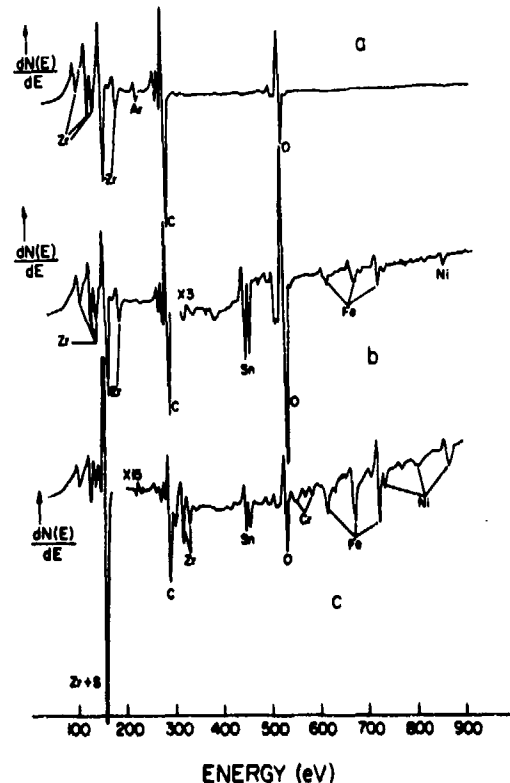


FIGURE 2. Auger spectrum $dN(E)/dE$ vs E for zircaloy-2 after 1-h argon-ion bombardment at 200- μ A bombardment current. (a) Room temperature; (b) 700°C; (c) 900°C.

brittle and strain rate sensitive, it appears reasonable that the formation of a brittle surface carbide layer at these temperatures is contributing to the decreased ductility. It is also suggested that the carbide present in the bulk is another factor influencing the decreased ductility at these temperatures. The presence of carbide in the bulk is clearly shown by the shape of the carbon peak¹⁶ in Fig. 2(a); this spectrum was taken after several surface layers had been removed from the sample by sputtering.

The known buildup of an oxide layer on zircaloy-2 above 300°C¹⁶ is in good agreement with the results of this work showing an increase in surface oxygen (following a decrease at lower temperatures) at temperatures above 300°C. This surface oxygen is undoubtedly diffusing from the bulk to the surface in our ultrahigh vacuum experimental setup. Naturally in an aqueous or other corrosive environment, the corrosive medium itself would also contribute to the buildup of this oxide layer. The low corrosion rates of zircaloy-2 below 300°C¹⁷ seem in good agreement with our results which show surface oxygen depletion at these temperatures. Up to 600°C, the outermost surface layer of zircaloy-2 has been shown in large part to consist of carbon in the form of a metal carbide, presumably zirconium carbide. Heating above 600°C removes this carbon from the surface and could

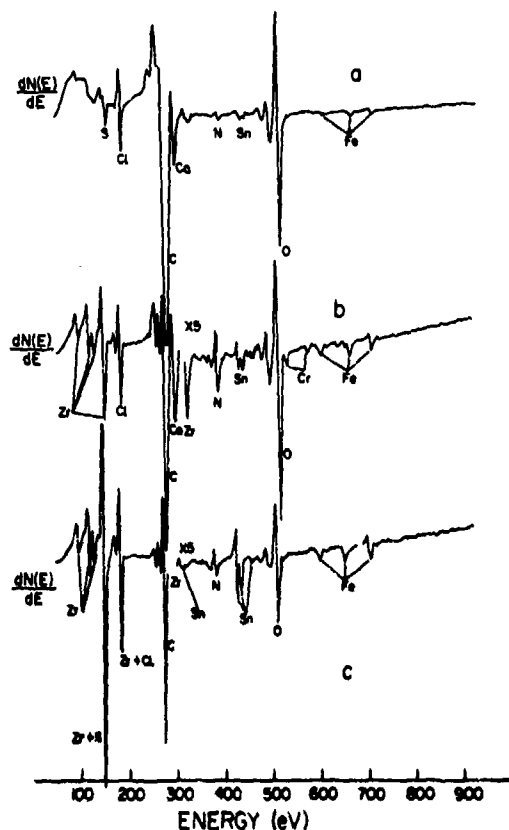


FIGURE 3. Auger spectrum $dN(E)/dE$ vs E for zircaloy-4 in the as-received condition. (a) Room temperature; (b) 300°C; (c) 750–800°C.

account for the marked decrease in hardness found by Lee¹⁸ above this temperature.

B. Zircaloy-4

The Auger spectrum of zircaloy-4 in the as-received condition was almost identical to that of zircaloy-2. That is to say, the surface contaminants present were the same, namely, carbon, oxygen, chlorine, and smaller amounts of nitrogen and sulfur. The room-temperature as-received spectrum of zircaloy-4 is given in Fig. 3(a). At high gains for this particular spectrum, tin and iron (no chromium) could be detected whereas this was not possible for both these elements in zircaloy-2, where only Fe was found at room temperature. As expected in this spectrum [Fig. 3(a)] taken at room temperature, no nickel could be detected since the bulk concentration was only 70 ppm. Carbon, at this temperature, was again present as free carbon. Heating zircaloy-4 to 200°C produced no noticeable changes in the Auger spectrum. When heated to 300°C, several facts became evident as shown in Fig. 3(b): The zirconium matrix peaks appeared and the oxygen peak decreased, much the same as for zircaloy-2. Nitrogen and tin were somewhat larger and the transitional carbon peak can be seen in the spectrum. Also, iron and chromium were

now detected whereas for zircaloy-2 they could not be at these relatively low temperatures. Iron detection for zircaloy-4 at these temperatures is not particularly surprising as zircaloy-4 normally contains more Fe than zircaloy-2 but the chromium detection here is noteworthy because the respective Cr contents of the two alloys are very nearly equal.

Heating zircaloy-4 to 750–800°C first of all brought large amounts of sulfur to the surface, see Fig. 3(c). The nitrogen peak was reduced, chromium removed completely, carbon (now as carbide) was diminished while the Sn and Fe peaks increased significantly. Thus, it appears that on the basis of the minor alloying components, there are distinct differences between the surface behavior of zircaloy-2 and zircaloy-4. Now after heating to between 900–950°C, in addition to the presence of very large sulfur and chlorine peaks, carbon was further reduced on the surface and the tin and oxygen were also reduced to roughly the same levels. But sizeable increases in both Cr and Fe were seen. This same trend held true to 1000°C with a fairly large triplet of iron peaks in evidence at this temperature. Sulfur and chlorine were still the largest peaks in the spectrum at this stage. Chlorine was removed from the surface of zircaloy-4 above 1000°C, but traces of Sn, Cr, and Fe could be found on the surface even at temperatures up to 1500°C. As with zircaloy-2, sulfur could not be removed from zircaloy-4 by heating alone to 1500°C in ultrahigh vacuum.

The results of a 1-h argon-ion bombardment on zircaloy-4 are given in Fig. 4(a). Once again fairly

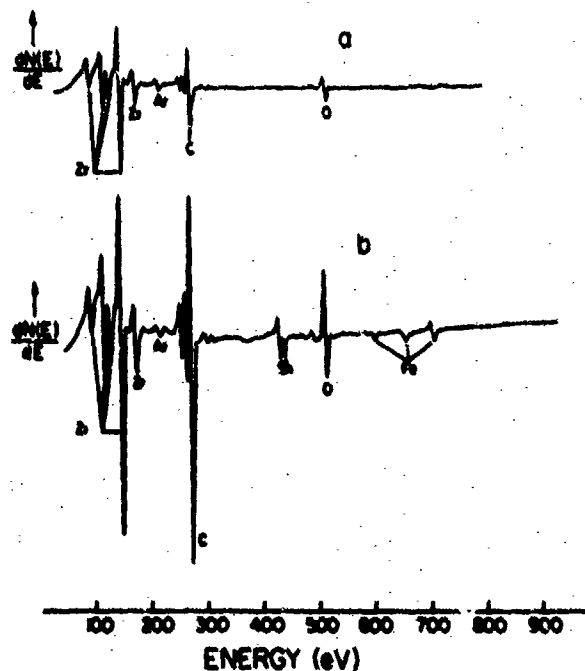


FIGURE 4. Auger spectrum $dN(E)/dE$ vs E for zircaloy-4 after 1-h argon-ion bombardment at 200-μA bombardment current; (a) Room temperature; (b) 700°C.

large peaks due to carbon and oxygen can be seen, indicating the presence of these impurities in the bulk. Again, possible CO contamination of the argon leading to the detection of carbon and oxygen in the spectrum of sputtered zircaloy-4 must be dismissed for the same reasons mentioned for zircaloy-2 and also because, from previous results in this laboratory,¹⁹ the shape of the carbon peak in both instances is indicative of a metallic carbide and not of chemisorbed CO. Very minor amounts of Sn could be found after bombardment but no Fe or Cr were present on the sputtered surface, nor were any traces of chlorine found. The absence of Cl on sputtered zircaloy-2 and zircaloy-4 surfaces indicates that this surface impurity is most likely introduced as part of the fabrication or cleaning steps rather than as part of the manufacturing process. Heating argon sputtered zircaloy-4 samples to 400°C produced very little change in the spectrum from that of the freshly bombarded surface. In fact, heating this surface to 600°C only caused a slight decrease in the oxygen peak size. Interestingly, sulfur had not begun to surface segregate even at temperatures of 600°C. But heating to 700°C [Fig. 4(b)] caused several things to happen. Oxygen and carbon were significantly decreased but tin and iron were now present on the surface in distinctly larger amounts than before. In fact, the Sn surface concentration was a maximum at this temperature. Judging from the shape of the spectrum in the 150-eV region (Zr has an Auger peak at 149 eV), it appeared that sulfur began to diffuse preferentially to the surface in the temperature range of 700–750°C. By 800°C sulfur predominated on the surface and virtually all oxygen was gone. Between 860 and 1200°C, the iron content on the surface did not appreciably increase, nor did the tin. At 1400°C, iron appeared to have its maximum surface concentration, but even at these high temperatures sulfur was still the predominant surface species.

A good deal of the bulk sulfur was removed from a zircaloy-4 sample by argon-ion bombarding the sample while holding it at 835°C. In this instance, tin was the predominant alloy species on the surface at temperatures up to 1400°C, while, with large amounts of sulfur present on the surface, iron was the major species found on the surface up to equally high temperatures. In this instance, the maximum Sn surface concentration occurred at 800°C.

Data on zircaloy-4 to use and compare with observed surface phenomena are less plentiful than for zircaloy-2. Zircaloy-4 does also possess strain rate sensitivity around 300°C²⁰ and it is suggested that this parameter is closely tied to surface carbide formation near these temperatures. The somewhat

better corrosion properties of zircaloy-4 over zircaloy-2 is no doubt related to the preferential surface segregation of Cr in zircaloy-4 over that of Cr in zircaloy-2. In zircaloy-2 in fact, Ni was seen to appear on the surface much more readily than Cr. This Cr on zircaloy-4 is likely to form a thin film of chromium oxide (rather than the usual zirconia) as has been reported by Baque *et al.*²⁰

III. Summary and Conclusions

There appear to be distinct differences in the surface segregation of the alloying components in zircaloy-2 and zircaloy-4. In general, the alloying constituents segregate more readily on zircaloy-4 before argon ion bombardment than on zircaloy-2 surfaces where they tend to segregate more readily after cleaning by argon sputtering. The segregation of carbon and subsequent metal carbide formation can be related to ductility minima at certain strain rates as can the behavior of surface oxygen to the formation of an oxide layer for both alloys. Zircaloy-4 has less tendency to adsorb carbon monoxide onto the surface than zircaloy-2 when both alloys simply remain in an ultrahigh vacuum for extended periods of time.

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